Controlling Non-Catalytic Decomposition of High Concentration Hydrogen Peroxide

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ABSTRACT

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent. High concentration H_2O_2 or High Test Peroxide (HTP) has been used extensively in the past in propulsion applications as mono and bipropellant. At low temperature, HTP can be catalytically decomposed to water and oxygen. Drawbacks to this approach include catalyst poisoning due to the presence of stabilizers in HTP, and susceptibility of the metal catalyst to melting because of the intense heat release. This renders the use of catalysts not only inconvenient but also quite expensive. An alternate approach for HTP decomposition is thermal, where no catalyst is required. HTP decomposition is accompanied by the production of enormous amount of heat that often leads to runaway reactions and subsequent explosion. **If the rate of thermal decomposition can be controlled, the ensuing technology would prove to be a viable and inexpensive alternative to using catalysts. This technology has the potential to replace any device that decomposes H2O2 catalytically. Also, the controlled thermal decomposer can be used as an accelerator to heat any substance quickly at the expense of very low power.** In order to control non-catalytic HTP decomposition, a deeper understanding of the chemical mechanism for H_2O_2 decomposition must be developed. The current work reports the development of detailed kinetic steps for HTP decomposition over a wide range of temperature and pressure. The resulting mechanism is then used to perform CFD simulations of a commercial HTP decomposer (patented by Pratt & Whitney) to explore safe operating conditions. A similar strategy can be applied to model COIL technology.

1.   INTRODUCTION

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent. High concentration H2O2 or High Test Peroxide (HTP) has been used extensively in the past in propulsion applications as mono and bipropellant. At low temperature, HTP can be catalytically decomposed to water and oxygen. Drawbacks to this approach include catalyst poisoning due to the presence of stabilizers in HTP, and susceptibility of the metal catalyst to melting because of the intense heat release. This renders the use of catalysts not only inconvenient but also quite expensive. An alternate approach for HTP decomposition is thermal, where no catalyst is required. HTP is a monopropellant whose decomposition is accompanied by the production of enormous amount of heat (85% HTP releases 586 cal/gm at 25°C) that often leads to runaway reactions and subsequent explosion. If the rate of thermal decomposition can be controlled, the ensuing technology would prove to be a viable and inexpensive alternative to using catalysts. In the past, efforts to control thermal decomposition have been unsuccessful primarily due to the lack of understanding about the chemical mechanism for H_2O_2 decomposition. Therefore, in order to control the decomposition, first the elementary reactions leading to water and oxygen, and the temperature and pressure dependence of their reaction rate constants must be known.

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14. ABSTRACT

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The ongoing MDA funded Phase I STTR is therefore aimed towards developing a detailed reaction mechanism for H_2O_2 thermal decomposition over a wide range of temperature and pressure. Computational fluid dynamics (CFD) simulations are then performed to calculate temperature profile within the reactor at various operating conditions. The results of the calculations some interesting conclusions on determining range of safe operating conditions for decomposition.

2. RESULTS AND DISCUSSION

2.1 Reaction Mechanism

Thermal decomposition of H_2O_2 is a complex process, and involves many intermediate radical species. Although, some theoretical and experimental works have been reported, a complete mechanism for H_2O_2 decomposition has so far has not been reported attempted. In the first part of our work, we have therefore developed a comprehensive mechanism for thermal decomposition of H_2O_2. Table 1 shows the complete mechanism and the rate constants for each reaction step.

*Table 1: Reaction mechanism for H_2O_2 decomposition. Rate constants are expressed in Arrhenius' form (see equation 1) with SI unit (kilomol, meter, second). **D**Hs are in Joule/kilomol. The "*«*" symbol represents that the backward reactions are also considered. M" represents third-body and reactions involving "M" are third-body mediated pressure dependent.*

	Reactions	A	n	Ea/R	ΔH
1	2O + M ↔ O2 + M	0.120E+12	-1.00	0.0	-4.9832E+08
2	O + H + M ↔ OH + M	0.500E12	-1.00	0.0	-4.2780E+08
3	O + H2 ↔ H + OH	0.387E+02	2.70	0.32E+04	8.1700E+06
4	O + HO2 ↔ O2 + OH	0.200E+11	0.00	0.0	-2.2237E+08
5	O + H2O2 ↔ OH + HO2	0.963E+04	2.00	0.20E+04	-6.1392E+07
6	O2 + H + M ↔ HO2 + M	0.280E+13	-0.86	0.0	-2.0543E+08
7	2O2 + H ↔ O2 + HO2	0.208E+14	-1.24	0.0	-2.0543E+08
8	O2 + H + H2O ↔ HO2 + H2O	0.113E+14	-0.76	0.0	-2.0543E+08
9	O2 + H ↔ O + OH	0.265E+14	-0.67	0.86E+04	-7.0519E+07
10	2H + M ↔ H2 + M	0.100E+13	-1.00	0.0	-4.3597E+08
11	2H + H2 ↔ 2 H2	0.900E+11	-0.60	0.0	-4.3597E+08
12	2H + H2O ↔ H2 + H2O	0.600E+14	-1.25	0.0	-4.3597E+08
13	H + OH + M ↔ H2O + M	0.220E+17	-2.00	0.0	-4.9914E+08
14	H + HO2 ↔ O + H2O	0.397E+10	0.00	0.34E+03	-2.2319E+08
15	H + HO2 ↔ O2 + H2	0.448E+11	0.00	0.54E+03	-2.3054E+08
16	H + HO2 ↔ 2 OH	0.840E+11	0.00	0.32E+03	-1.5185E+08
17	H + H2O2 ↔ H2 + HO2	0.121E+05	2.00	0.26E+04	-6.9562E+07
18	H + H2O2 ↔ OH + H2O	0.100E+11	0.00	0.18E+04	-2.8458E+08
19	OH + H2 ↔ H + H2O	0.216E+06	1.51	0.17E+04	-6.3171E+07
20	2OH + M ↔ H2O2 + M	0.740E+08	-0.37	0.0	-2.1456E+08

21	2OH $\leftrightarrow$ O + H2O	0.357E+02	2.40	-0.11E+04	-7.1341E+07
22	OH + HO2 $\leftrightarrow$ O2 + H2O	0.145E+11	0.00	-0.25E+03	-2.9371E+08
23	OH + H2O2 $\leftrightarrow$ HO2 + H2O	0.200E+10	0.00	0.21E+03	-1.3273E+08
24	OH + H2O2 $\leftrightarrow$ HO2 + H2O	0.170E+16	0.00	0.15E+05	-1.3273E+08
25	2HO2 $\leftrightarrow$ O2 + H2O2	0.130E+09	0.00	-0.82E+03	-1.6097E+08
26	2HO2 $\leftrightarrow$ O2 + H2O2	0.420E+12	0.00	0.60E+04	-1.6097E+08
27	OH + HO2 $\leftrightarrow$ O2 + H2O	0.500E+13	0.00	0.87E+04	-2.9371E+08

The reaction steps and their rate constants are compiled from GRI-Mech 3.0 for hydrocarbon combustion. The hydrocarbon combustion mechanism has been tested over the years by many researchers and appears to be accurate. The steps related involving hydrogen and oxygen only were selected from the GRI-Mech mechanism for building H_2O_2 decomposition mechanism. The important feature of the mechanism is the pressure dependence of the reaction rate. In real situation, the pressure inside the decomposer is likely to vary widely. Therefore in order to model a reacting flow accurately, the reaction rate constants must reflect their pressure dependence. The reaction mechanism in Table 1 shows that many reactions are pressure dependent (or third-body mediated). One of the most important reactions in the list is the step number 20. This reaction represents the first step of H_2O_2 decomposition to produce two OH radicals. The OH radicals initiate other reactions and produce some intermediate species, such as HO2, H and O.

2.2 CFD Simulation of Decomposition

Choice of H_2O_2 Decomposer Geometry:

Figure 1 shows a HTP decomposer patented by Pratt & Whitney (W.B. Watkins; Patent # US 6,532,741 B2; March 18, 2003). The decomposer first catalytically decomposes HTP in a chamber marked as 'A'. Additional HTP is introduced via secondary injectors (323 and 319) into the chamber 'B'.
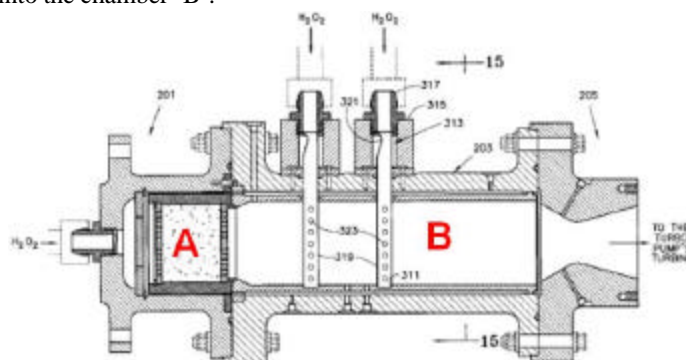

Figure 1: A typical H_2O_2 decomposer. Chamber 'A' decomposes catalytically while chamber 'B' thermally with heat from catalytic decomposition.

The HTP in chamber 'B' decomposes non-catalytically by using the heat generated by catalytic HTP decomposition in chamber 'A', and the decomposition products pass

through the nozzle. In our present parametric study, we have used a geometry which is similar to chamber 'B' in Figure 1. The geometry has immediate relation to an existing commercial design, and was, therefore, deemed more relevant to the current study. Figure 2 shows the computational grid and dimension of the model. It should be pointed out that the patent by Pratt & Whitney did not report the exact dimension of the prototype. We have made an educated guess for the dimensions of chamber 'B' and any match of dimensions with the exact patented geometry should be considered a coincidence.
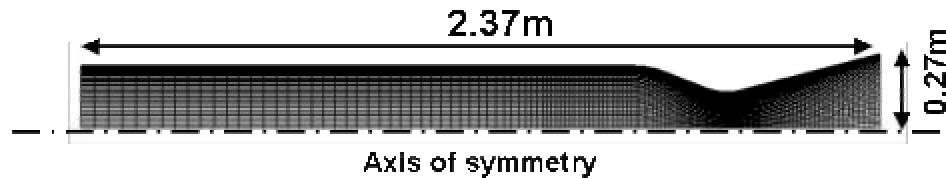

Figure 2: Geometry of the tube decomposer used for CFD simulations. This resembles chamber 'B' in Figure 1.

In the following sections, we outline the computational model used for H_2O_2 decomposition. The primary goal is to perform parametric study with respect to inlet temperature and H_2O_2 concentration, and calculate temperature distribution within the reactor. Based on the simulation results, some preliminary recommendations will be made to avoid hazardous situations.

Computational Model

Computational fluid dynamics (CFD) techniques were used to perform the necessary simulations. These simulations were performed using the commercial CFD software, CFD-ACE+. A brief description of the pertinent physical models used in this study follows:

Fluid Flow: The compressible Navier-Stokes Equations were solved using the SIMPLEC algorithm after finite-volume discretization. The ideal gas law was used to compute the density of the gas-mixture.

Turbulence: Turbulence was modeled using the standard k-ε model.

Radiation: The decomposition of HTP produces high temperature. Coupled with the fact that the operating pressure is several atmospheres and that a large amount of water vapor is generated during the decomposition process, it is important to take into account radiative loss from the participating hot gases, and the absorption of radiation in the colder parts and walls. Radiative transport was modeled using the Discrete Ordinates Method. Planck-mean absorption coefficients of the individual species (mainly water vapor and H_2O_2), computed from the HITEMP database, were used for calculation of the absorption coefficient of the gas mixture. These coefficients were computed locally based on the local temperature, pressure and concentrations of the various species.

Chemical Kinetics: An advanced algorithm, which is capable of robustly handling stiff chemical kinetics, was used to couple chemical reactions with transport.

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Transient Parametric Study

 One of the most important aspects is to examine the maximum temperature in the reactor before steady state is reached. It is possible that transient temperature is much higher than that of steady state, and the conclusions based on only steady state calculations may be misleading.   Therefore, we performed transient simulations with at various operating condition to calculate the maximum temperature. In these simulations vapor phase of 98% HTP is injected through the inlet at various temperature. Table 1 shows the parameters that are used for CFD simulations.

Table 1: Operating conditions and physical models used in the CFD simulations.

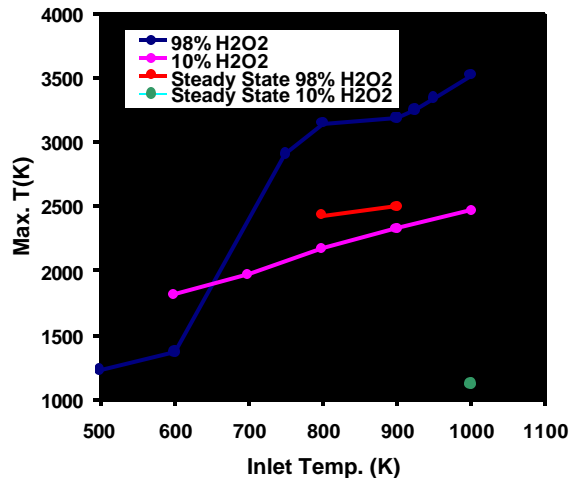| Fixed Parameters	
Inlet pressure	200 atmosphere
Inlet flow rate	Approximately 1700kg/sec
Wall boundary condition	Adiabatic and external heat transfer
Variable parameters	
Inlet temperature	500K to 1000K
Inlet concentration	98%, 50%, 30%,10%
Models	
Physics models	Heat transfer, flow, chemical reaction, turbulence and radiation.

Figure 3: Results of parametric studies as a function of inlet temperature at two different H_2O_2 dilutions, namely 98% and 10%. The inlet temperature is the resultant temperature when water vapor and H_2O_2 vapor mixed at two different temperatures before entering through the inlet.

Figure 3 shows the results of our simulations with 98% and 10% H_2O_2. Lower concentration of H_2O_2 essentially means that pure H_2O_2 has been premixed with water vapor so that water vapor is used as diluent. In all cases, for simplicity, it is assumed that

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the reactants are in the vapor phase, although a jet of atomized liquid is injected in real cases. Therefore the calculated temperature in the CFD simulations should be considered at upper bound due to non-inclusion of latent heat of vaporization of the liquid before decomposition. This mixture is then fed through the inlet of the decomposer. Simulations have been performed at various inlet temperatures. Here the inlet temperature is the effective temperature when pure H_2O_2 vapor at a particular temperature is mixed with water vapor at another temperature. We assume that the mixed gases enter the inlet with the effective temperature. Figure 3 shows that the maximum temperature during the transient simulations of 98% H_2O_2. At lower inlet temperatures, the maximum temperature is quite low, and the decomposition does not start. However, the maximum temperature is always higher than the inlet temperature, and location of maximum temperature is at the wall near the nozzle. This is due to the high viscous dissipation. At that region, Mach number varies from zero at the wall to 2.2 within 3 mm from the wall. This leads us to conclude that although there is hardly any H_2O_2 decomposition at lower temperature, effective wall cooling is necessary in order to prevent material degradation. We consider this to be one of the most important aspects one needs to consider for high-speed flow. Above 750K, decomposition of 98% H_2O_2 starts vigorously and in an uncontrollable manner. At the stage the wall and gas temperatures are nearly the same. *Although the gas temperature is very high, it is the high wall temperature of the decomposer that will lead to material failure.* In order to cool the wall, we performed simulation by incorporating heat loss from the wall to atmosphere by radiation and natural convection. However, results show no appreciable decrease of wall temperature. Therefore natural heat loss may not be adequate to cool the wall, and active cooling of wall is necessary, such as cold water jacket, in order to prevent material failure at all inlet temperatures when the decomposer is operated at mass flow rate and pressure as shown in Table 1.

When the lower concentration of H_2O_2, such as 10%, is used, there is no decomposition till inlet temperature of 1000K. However, as discussed above, the wall temperature reaches very high due to viscous dissipation. Steady state calculations at 1000K show (Figure 3) that the wall cools down due to transfer of heat to the gas. We are in process of calculating maximum temperature at other inlet temperatures for lower H_2O_2 concentrations.

Steady State Parametric Study
An ideal decomposer will be able to decompose H_2O_2 constantly without generating too much of heat at the steady state while the maximum wall temperature should not be too high during the transient period. In case of 98% H_2O_2, the decomposition does not occur when wall temperature is within acceptable limit. When the decomposition occurs, the temperature becomes uncontrollable. On the other hand, 10% H_2O_2 does not decompose till inlet temperature reaches 1000K. We are therefore in search of a particular concentration of H_2O_2 for which the decomposition is controllable. Figure 4 shows our steady state simulation of decomposition of few different concentrations of H_2O_2 at 1000K inlet temperature. The 10% H_2O_2 hardly decomposes and the maximum temperature (at steady state) remains close to the inlet temperature. Slight rise is temperature is due to compression. The 30% H2O2 decomposes significantly and

maximum temperature is within acceptable limit. As the H_2O_2 concentration increases, the maximum steady state temperature also increases, and H_2O_2 starts decomposing very close to the inlet. The transient calculations for these cases are in progress in order to examine the maximum temperature of the wall and the gas.
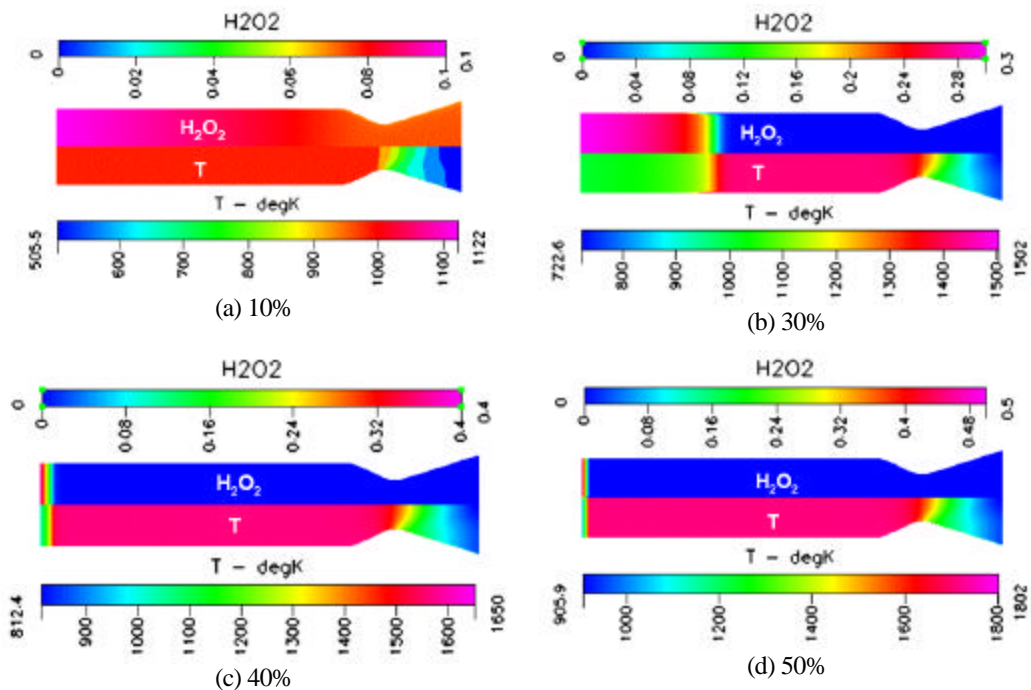

Figure 4: Steady state temperatures and H_2O_2 decomposition at various dilutions.

3.   SUMMARY AND CONCLUSIONS

Non-catalytic decomposition of hydrogen peroxide has been studied using CFD technique in order to find out root cause of hazardous situations, and its remedy. A comprehensive mechanism is first developed in order to understand fundamental characteristics of thermal H_2O_2 decomposition. The important feature of this mechanism is the inclusion of pressure dependence into the rate constants. This mechanism is then used to perform transient and steady state CFD simulations. Results suggest that the wall temperature reaches very high before the system evolves to the steady state, and active cooling is essential in order to avoid material failure and catastrophic situation. Steady state simulations suggest that it is possible to tailor the steady temperature by adjusting inlet temperature and H_2O_2 dilution. However, more transient simulations are necessary to confirm that the maximum transient temperature is not too high.

4. IMPLICATIONS

Due to the environment friendly nature, hydrogen peroxide has recently attracted much attention. One of the most relevant areas where the current work can be applied is Airborne Laser (ABL). Since the chemistry play a major role in COIL technology in ABL, the similar to the above strategy can be applied to develop a detail mechanism for singlet oxygen generation. CFD simulations can then be used in conjunction with the mechanism to predict laser performance. Recently, MDA is interested in replacing Halon with water to extinguish the onboard fire due to H_2O_2 spill from the ABL system. The above mechanism can be directly used in CFD simulations to design an extinguishing system.

5. ACKNOWLEDGMENTS